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Bendix® Transportable Field Calibration System, Models 8861D and 8861DA

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The purpose of this report is to aid calibration personnel in performing calibrations and audits in exactly the same manner with identical calibration systems. One of the advantages of the procedures is that chemiluminescence ozone analyzers can be calibrated or audited in the field without the bulky equipment required for the neutral buffered potassium iodide calibration procedure. A second advantage is that more precise results can be obtained.

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OZONE CALIBRATION AND AUDIT BY GAS PHASE TITRATION IN EXCESS OZONE
(Bendix® Transportable Field Calibration System, Models 8861D and 8861DA)

by

Thomas A. Lumpkin and Barry E. Martin
Field Studies Section
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

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ABSTRACT

Detailed procedures for the dynamic calibration and audit of chemiluminescence ozone analyzers are presented. These procedures were developed and applied within the Environmental Monitoring Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. The purpose of the procedures is to aid calibration and audit personnel in performing calibrations and audits in exactly the same manner with identical calibration systems.

The calibrations and audits are performed by means of a gas phase titration technique utilizing the rapid gas phase reaction between nitric oxide and ozone with excess ozone present. The nitric oxide is generated by using a cylinder of nitric oxide in nitrogen that has been standardized against a National Bureau of Standards Standard Reference Material. The instrument being calibrated or audited must have a linear response to ozone. An ozone concentration is generated using a dynamic calibration system (Bendix® Model 8861D or 8861DA) and is introduced to the analyzer under calibration or audit to obtain an up-scale response. A known concentration of nitric oxide is added to excess ozone in the calibration system and the change in analyzer response noted. Under specifically controlled conditions, the decrease in analyzer response is equal to both the concentration of ozone consumed and the concentration of nitric oxide added. The original ozone concentration (before nitric oxide was added)

can then be calculated. Other calibration concentrations of ozone can be obtained by diluting the original ozone concentration and repeating the gas phase titration.

One of the advantages of these procedures is that chemiluminescence ozone analyzers can be calibrated or audited in the field without the bulky equipment required for the neutral buffered potassium iodide calibration procedure. A second advantage is that more precise results can be obtained. A standardized cylinder of nitric oxide replaces the potassium iodide solution, the set of bubblers, the vacuum system, and the spectrophotometer required for the potassium iodide method.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cm^3	— cubic centimeter
GPT-O_3	— gas phase titration in excess ozone
hr	— hour
l	— liter
min	— minute
mol	— mole
NBKI	— neutral buffered potassium iodide
NBS	— National Bureau of Standards
ppm	— parts per million
psig	— pounds per square inch gauge
s	— second
SRM	— Standard Reference Material
URL	— upper range limit

SYMBOLS

N_2	— nitrogen
NO	— nitric oxide
NO_2	— nitrogen dioxide
NO_x	— total oxides of nitrogen
O_2	— oxygen

O_3	– ozone
P_A	– Input A pressure gauge setting
P_B	– Input B pressure gauge setting
P_C	– Input C pressure gauge setting
I_3^-	– triiodide ion
C_{NO}	– cylinder NO concentration, ppm
F_G	– flow through O_3 generator, cm^3/min
F_{NO}	– NO flow rate, cm^3/min
F_0, F_1, F_2	– total dilution air flows, cm^3/min
I	– analyzer recorder response after addition of NO to system, % chart
I_{80}, I_{40}, etc.	– analyzer recorder response to O_3, % chart
$I_{80}(A)$, $I_{40}(A)$, etc.	– adjusted analyzer recorder response to O_3, % chart
$[O_3]_{80}$, $[O_3]_{60}$, etc.	– O_3 concentration at URL of 80%, 60%, etc., ppm
$(PAE)_{80}$, $(PAE)_{60}$, etc.	– percent audit error at URL of 80%, 60%, etc.
Z_A	– adjusted analyzer recorder response, % chart
Z_U	– unadjusted analyzer recorder response, % chart

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The personnel of the Field Studies Section, Environmental Monitoring Branch, contributed important input after testing and using the procedures. Special recognition is due Mr. Kenneth Rehme and Mr. Frederick Smith of the Monitoring Techniques Evaluation Section, Environmental Monitoring Branch, for the initial testing and evaluation of the gas phase titration in excess ozone technique.

SECTION 1

INTRODUCTION

The Federal Register specifies the neutral buffered potassium iodide (NBKI) method as the procedure for calibration of designated reference methods for measurement of photochemical oxidants (1). This procedure consists of passing a generated ozone (O_3) concentration through a NBKI solution and then measuring the triiodide ion (I_3^-) concentration with a calibrated spectrophotometer. The O_3 concentration can be determined from the I_3^- concentration and the known volume of air passed through the NBKI. The basic equipment is an O_3 generator, a dilution air supply, a flowmeter, a bubbler train, a vacuum system, and a spectrophotometer. Commercially available calibration systems usually combine a dilution air supply with an O_3 generator. The remaining equipment can become difficult to manage and operate on field calibrations, especially if air travel is involved. Often, due to lack of proper facilities, the NBKI procedure cannot be performed as precisely in the field as in the laboratory. Also, the spectrophotometer may require recalibration after being moved from place to place in the field. Recalibration of the spectrophotometer involves exact standards and is difficult to accomplish under field conditions.

This report describes procedures for performing O_3 calibrations and audits. These procedures — gas phase titration in excess ozone — utilize a standard

nitric oxide (NO) gas cylinder as the reference standard. The only other equipment necessary is a flowmeter and a calibration system capable of supplying specified stable O_3 concentrations at specified flow conditions. Although a significant difference exists between these procedures and the NBKI procedure, the difference is consistent. Thus the procedure can be referenced to the NBKI procedure specified in the Federal Register.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Using these procedures, the calibration and audit of O_3 analyzers requires less complicated equipment than with the NBKI procedure. In addition, more consistent and more precise results can be obtained in the field. These procedures have been used successfully by the Environmental Monitoring Branch on two previous studies: the 1975 Summer Ozone Study and the 1976 Washington, D.C. Oxidant-Hydrocarbon Study. The procedures are presently being used on the National Forest Ozone Study which began in 1976.

Although the procedures have been written for a modified Bendix® Model 8861D or a Bendix® Model 8861DA Transportable Field Calibration System, any comparable calibration system can be used by modifying the procedures slightly. Any different calibration system must be thoroughly tested and shown to be consistent with the NBKI procedure.

SECTION 3

PRINCIPLE

Ozone calibration by gas phase titration in excess ozone (GPT-O_3) is based upon the rapid gas phase reaction between O_3 and NO in accordance with the following equation (1,2):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad k = 1.0 \times 10^7 \text{ l/mol s}$$

An O_3 concentration of unknown magnitude is generated in a dynamic calibration system and sufficient NO of known concentration is added to decrease the O_3 concentration by 90-95% of its original value as measured on an uncalibrated chemiluminescence O_3 analyzer. If the exact NO concentration is known, the concentration of O_3 can be determined and can then be used to calibrate the O_3 analyzer. The standardization of the NO cylinder used in this technique is based on direct comparison with a certified National Bureau of Standards (NBS) NO Standard Reference Material (SRM). The flow conditions used in the dynamic calibration system are optimized to ensure the quantitative reaction of NO with O_3 and to minimize the reaction of nitrogen dioxide (NO_2) and O_3 which can lead to errors in the calibration procedure. Erroneous results will also occur if the analyzer response is nonlinear. The analyzer linearity is verified by a dilution technique described in Section 6.

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SECTION 4

APPARATUS

BENDIX® TRANSPORTABLE FIELD CALIBRATION SYSTEM, MODEL 8861D OR MODEL 8861DA

Figures 1 and 2 illustrate Bendix® Models 8861D and 8861DA, respectively. The Model 8861D system should be modified as described below and as shown in the flow diagram in Figure 3. In Figure 3, the modified sections are enclosed in broken lines. The modifications make the calibration system more effective and versatile in calibrating and auditing O_3 analyzers by these procedures.

Modification of Bendix® Model 8861D

Step 1—

Replace the 0-15 psig NO pressure gauge with a 0-25 psig gauge. Dismantle the O_3 generator-flow capillary compartment and replace the NO flow capillary with one that will give a flow rate of about 20 cm^3/min at 25 psig. This modification allows higher concentrations of NO to be obtained from the calibration system at the specified dilution flow rates.

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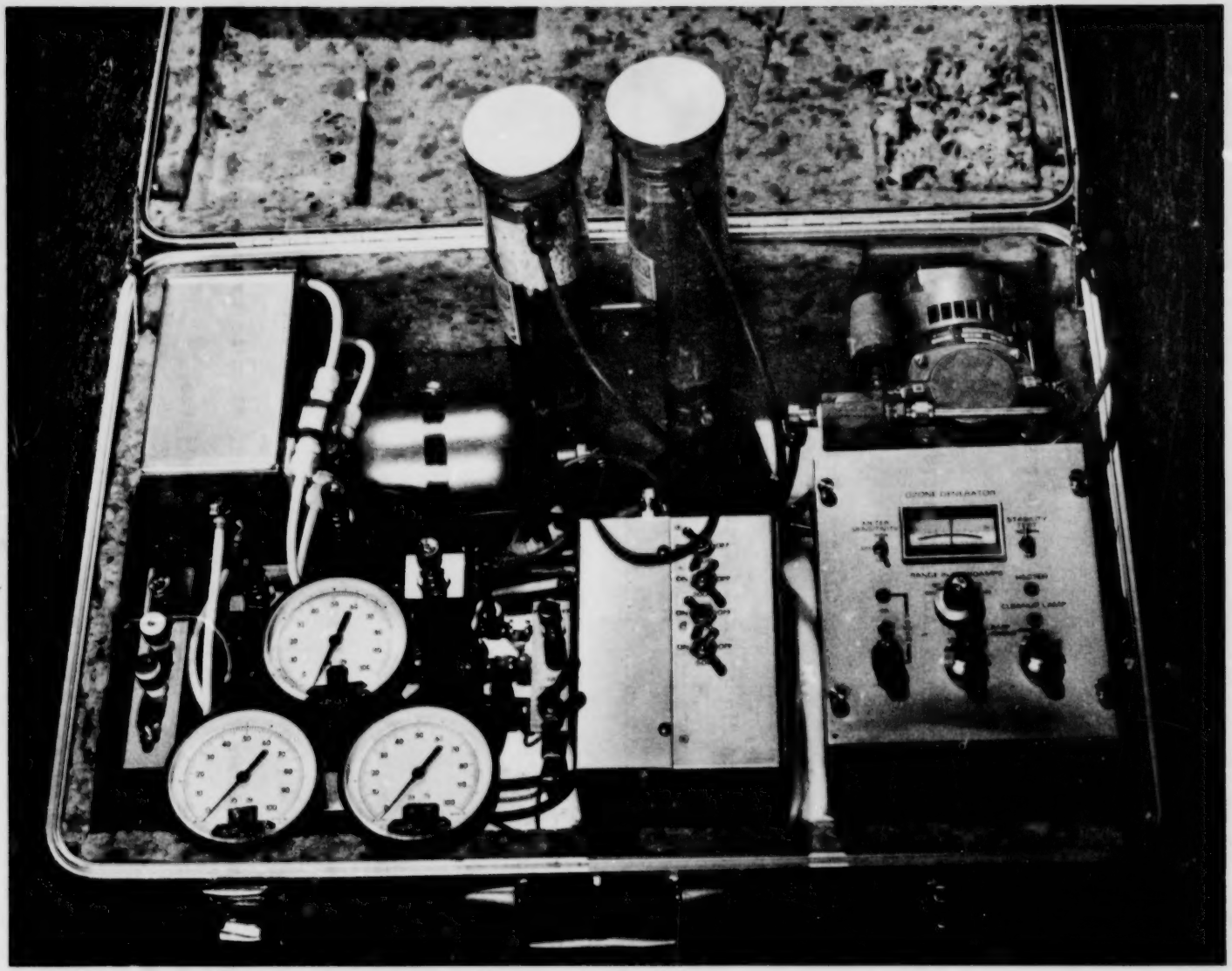

Figure 1. Modified Bendix® Model 8861D Transportable Field Calibration System.

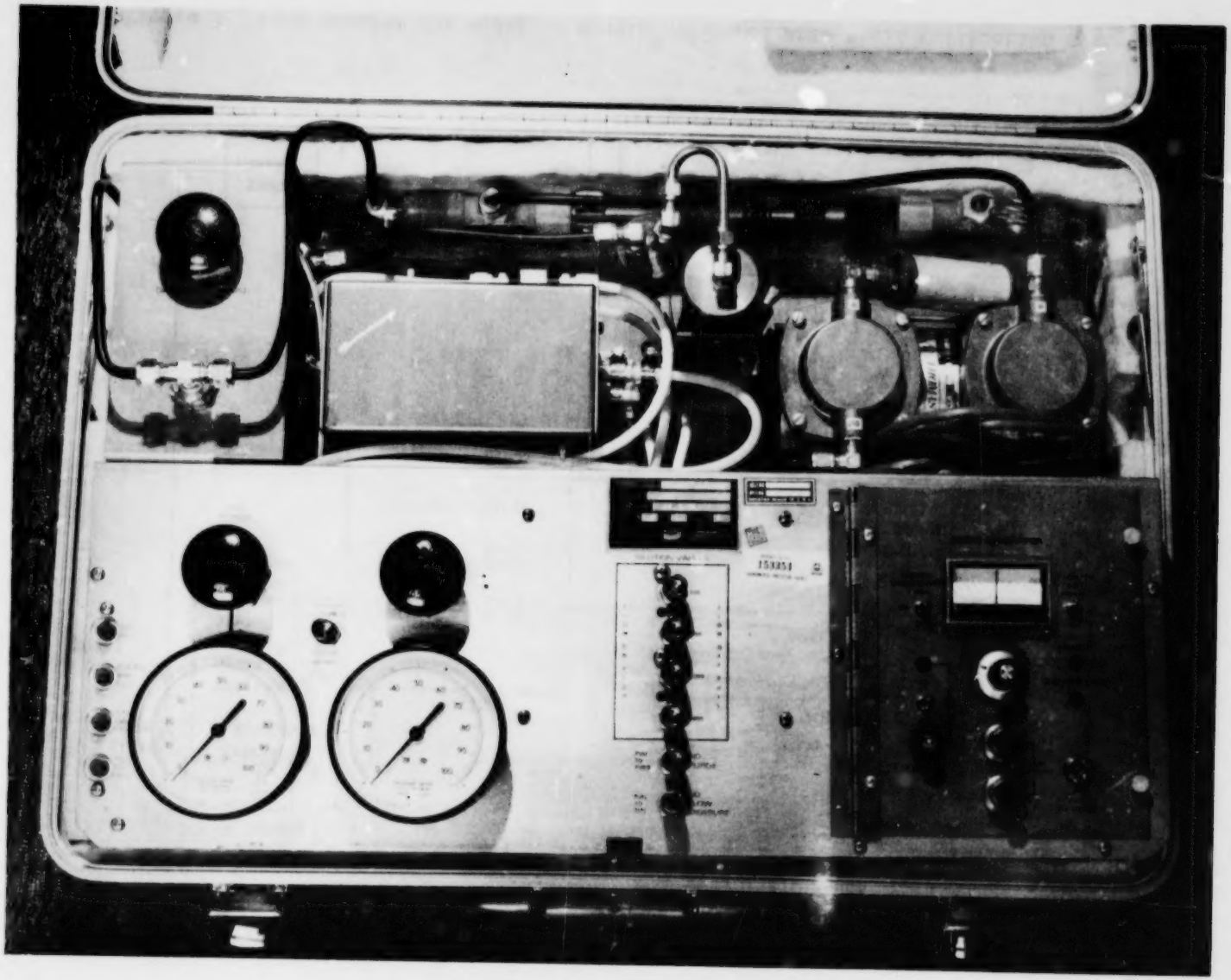

Figure 2. Bendix® Model 8861DA Transportable Field Calibration System.

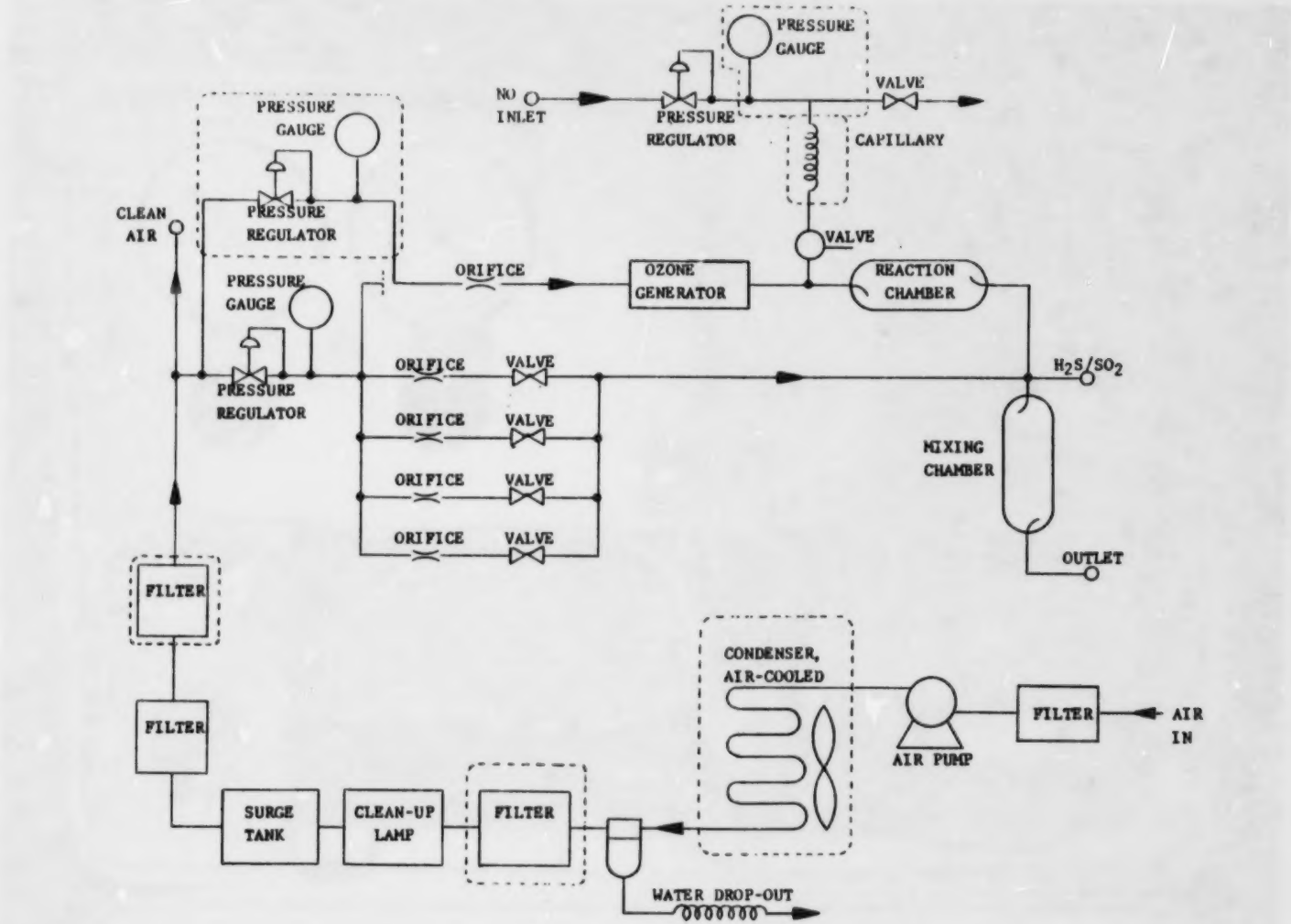

Figure 3. Flow Diagram for modified Bendix® Transportable Field Calibration System.

Step 2–

While the compartment is dismantled, remove the orifice fitting that controls the flow through the O_3 generator and plug the hole from which the fitting was removed. Replace the fitting at the inlet to the O_3 generator with the orifice fitting. Connect an 18-in length of 1/8-in o.d. Teflon® tubing to the orifice fitting. Close the compartment, leaving the free end of the Teflon® tubing outside the compartment. Connect an additional pressure regulator and gauge (0-25 psig, preferably similar to original equipment) to the zero air supply upstream from the existing regulator and gauge that control the dilution air flow. Connect the Teflon® tubing to the outlet of the pressure regulator just installed. This modification allows the flow through the O_3 generator to be controlled separately by the new regulator and gauge. The modification is needed primarily for calibrations and audits of O_3 analyzers by the GPT-O_3 procedure. Although the modification is not essential for calibrations and audits of $NO/NO_2/NO_x$ analyzers, the system can still be used to calibrate such analyzers.

Step 3–

Remove the condensing coil from the system. Cut the electrical wires to the fan and remove it from the system. Insulate the ends of the cut wires. Install a silica gel scrubber (0.5 l or larger capacity) in line between the water dropout and the cleanup lamp. This modification gives a drier calibration air than that obtained with the condenser-fan assembly.

Step 4–

Replace the small charcoal-soda lime filter downstream from the surge tank with one with a capacity of at least 0.5 l. This will allow the calibration system to be operated for a longer time between scrubber material changes.

O_3 ANALYZER

Any chemiluminescence O_3 analyzer that has a rapid and linear response to O_3 can be calibrated by this technique. Ozone analyzers using other measurement principles can be calibrated if they do not respond to NO or NO_2.

FLOWMETER

A bubble flowmeter kit and/or a wet-test meter capable of measuring absolute flow rates between 1 and 5000 cm^3/min is required.

PRESSURE REGULATOR

The standard NO cylinder requires a pressure regulator with stainless steel internal parts and Teflon® seats.

SAMPLE MANIFOLD

A Kjeldahl mixing bulb (approximately 300 cm^3 volume) with a multiport glass manifold is recommended.

SECTION 5

REAGENTS

STANDARD NO CYLINDER

The cylinder should contain approximately 100 ppm NO in nitrogen (N_2). The NO content of the cylinder is determined by comparison with a NBS NO SRM.

ZERO AIR

The Bendix® Model 8861 Transportable Field Calibration Systems supply air free of contaminants that would cause a detectable response in the O_3 analyzer or interfere with the O_3 calibration. The zero air supply of the Model 8861D System should include two scrubbing columns; the first column should contain indicating silica gel and the second should contain 1/2 soda lime and 1/2 activated charcoal, in that order. These two scrubbing columns should be replaced after 8 hr of actual use, or sooner (if indicated by the silica gel). The Model 8861DA System should have one scrubbing column containing 1/2 soda lime and 1/2 activated charcoal, in that order. This column should be replaced after 8 hr of actual use.

SECTION 6

CALIBRATION PROCEDURE

The flow conditions in the Bendix® Model 8861 Transportable Field Calibration Systems are optimized for this procedure and must be duplicated precisely to ensure the validity of the calibration.

STEP 1

Record pertinent information about the analyzer being calibrated in the space provided on the data sheet (see Appendix A). If a request for information does not apply, write "N/A" in the space. In the margins, record any pertinent information needed for a particular analyzer but not specifically requested on the data sheet. Adjust all analyzer flow rates to the manufacturer's specifications.

STEP 2

Connect the standard NO cylinder to the Bendix® calibration system. Open the cylinder valve and let the NO flow rate stabilize. The pull-to-test valve for NO should be out while the O_3 generator and dilution air flow rates are measured. Place the sample manifold on the outlet of the calibration system.

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(See Figure 4 for the arrangement of the calibration apparatus.) Switch capillaries 1, 2, 3, and 4 of Input C (dilution air) to the "OFF" position. Set the air flow through the O_3 generator to 150-200 cm^3/min by adjusting the Input A gauge pressure. Measure the flow using a bubble flowmeter attached to the outlet of the calibration system. (The sample manifold must be disconnected each time a flow measurement is made at the outlet of the system.) Record the O_3 generator air flow (F_G) and the Input A pressure gauge setting (P_A) on the data sheet.

STEP 3

Set the total air flow to approximately 2500 cm^3/min by adjusting the Input C gauge pressure (any combination of capillaries 1, 2, 3, and 4 can be used). Using a bubble flowmeter or wet-test meter, measure the total air flow at the outlet of the calibration system. Record the total air flow (F_O), Input C pressure gauge setting (P_C), and capillaries used on the data sheet.

STEP 4

Advance the O_3 analyzer recorder chart a few inches from the last ambient air trace and allow the analyzer under calibration to sample its internal zero air (if applicable) until a stable response is obtained. Then allow the analyzer to sample calibration zero air until a stable response is obtained. Record the unadjusted recorder response (Z_U) for the analyzer's zero and for calibration zero air. Make the proper zero adjustment to the analyzer using

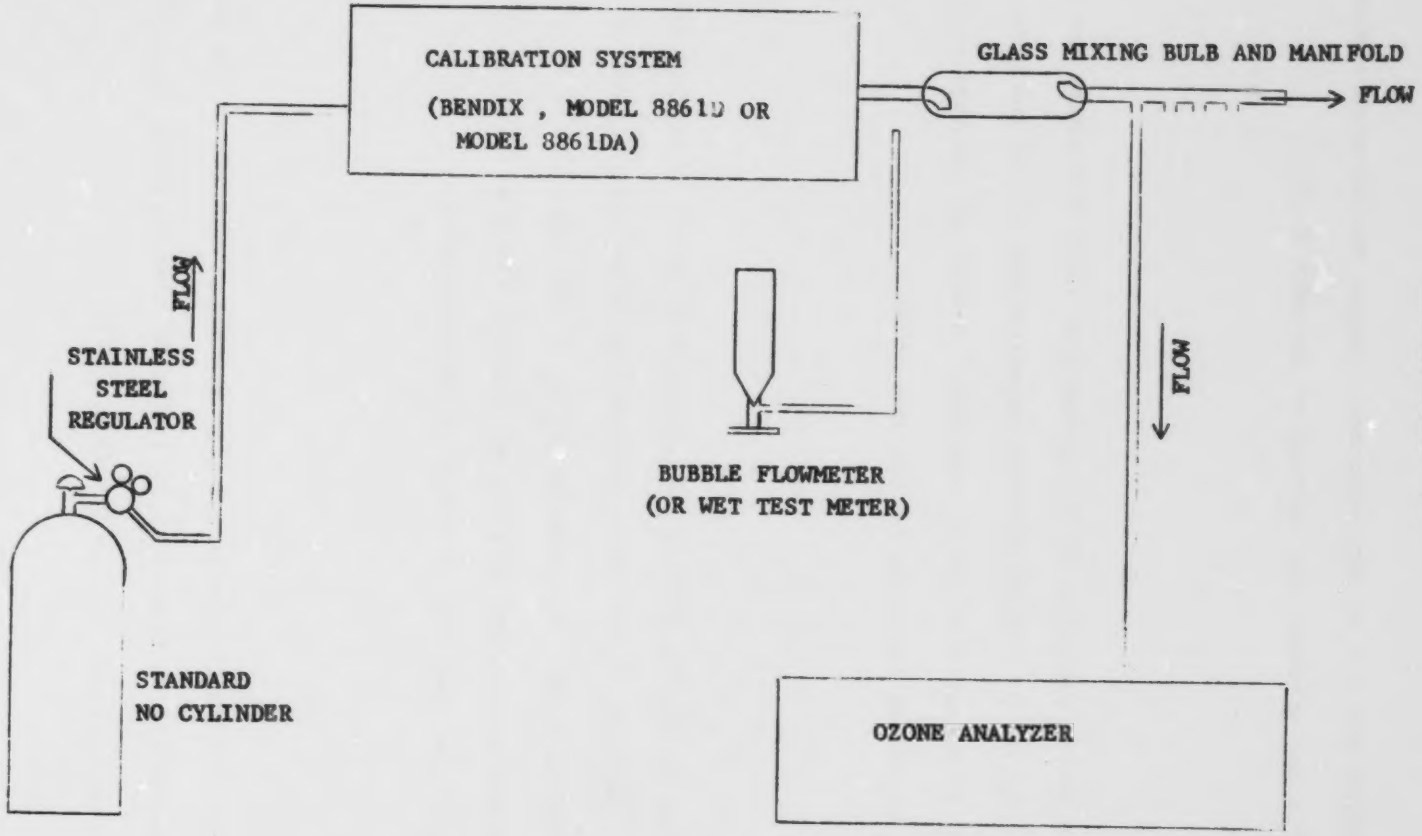

Figure 4. Flow scheme for calibrations and audits by gas phase titration in excess ozone.

the calibration zero air as the reference. Record the adjusted recorder response (Z_A) and adjusted zero setting on the data sheet.

STEP 5

Switch the O_3 generator to the appropriate range and adjust the set point dial to provide an O_3 concentration of approximately 80% of the upper range limit (URL) as measured on the O_3 analyzer. Record the analyzer response (I_{80}) and the O_3 generator set point on the data sheet.

STEP 6

Add the NO flow by pushing the pull-to-test valve in and adjust the Input B pressure regulator until the O_3 analyzer response has decreased by 90-95% of its original value. For example, if I_{80} = 85% chart and Z_A = 5% chart, the NO flow should be adjusted to yield an analyzer response of 9-13% chart. Record the analyzer response (I) after it has stabilized.

STEP 7

Measure the NO flow using a bubble flowmeter attached to the pull-to-test valve. Record the NO flow (F_{NO}), cylinder NO concentration (C_{NO}), and Input B pressure gauge setting (P_B) on the data sheet.

STEP 8

Calculate the exact NO concentration from:

$$[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} \qquad \text{(Eq. 1)}$$

where $[NO]$ = NO concentration, ppm

F_{NO} = NO flow, cm^3/min

C_{NO} = cylinder NO concentration, ppm

F_O = total air flow, cm^3/min

Record the calculations on the data sheet.

STEP 9

Calculate the O_3 concentration from:

$$[O_3]_{80} = \frac{I_{80} - Z_A}{I_{80} - I} \times [NO] \qquad \text{(Eq. 2)}$$

where $[O_3]_{80}$ = 80% URL O_3 concentration, ppm

$[NO]$ = NO concentration, ppm

I_{80} = original O_3 analyzer response, % chart

I = O_3 analyzer response after addition of NO, % chart

Z_A = adjusted zero air recorder response, % chart

Calculate the response to which the recorder should be adjusted as follows:

$$I_{80}(A) = \frac{[O_3]_{80} \times 100}{URL} + Z_A \qquad \text{(Eq. 3)}$$

where $I_{80}(A)$ = adjusted recorder response, % chart

URL = upper range limit, ppm

Record the calculations on the data sheet.

STEP 10

With the NO flow removed, the O_3 analyzer response should return to its original value (I_{80}). If the response does not return to within ± 1% chart of I_{80}, recheck I by adding NO to the system again. If I is exactly the same as before, remove the NO and let the O_3 response return to its new value. Record this new response as I_{80} and recalculate $[O_3]_{80}$ and $I_{80}(A)$. If I is not the same as before, measure the NO flow again and recalculate [NO], $[O_3]_{80}$, and $I_{80}(A)$. After the O_3 response has stabilized up-scale, record this new value as I_{80}. Adjust the span control until the analyzer recorder gives the desired response as calculated in Equation 3. Record the adjusted recorder response [$I_{80}(A)$] and adjusted span setting on the data sheet.

STEP 11

Adjust the Input C gauge pressure to give a total air flow of approximately 3300 cm^3/min. Using a bubble flowmeter or wet-test meter, measure the total

air flow at the outlet of the calibration system. Record the total air flow (F_1), Input C pressure gauge setting (P_C), and the capillaries used on the data sheet. Calculate the diluted O_3 concentration at 60% URL ($[O_3]_{60}$) from:

$$[O_3]_{60} = [O_3]_{80} \times \frac{F_O}{F_1} \qquad \text{(Eq. 4)}$$

where $[O_3]_{60}$ = 60% URL O_3 concentration, ppm

$[O_3]_{80}$ = 80% URL O_3 concentration, ppm

F_O = original total air flow, cm^3/min

F_1 = total air flow after dilution, cm^3/min

Record the calculations and the recorder response (I_{60}) on the data sheet.

STEP 12

Readjust the Input C gauge pressure to give the original total air flow (F_O). Repeat Steps 5 through 10, substituting 40% URL for 80% URL, I_{40} for I_{80}, and $[O_3]_{40}$ for $[O_3]_{80}$. Disregard the reference in Step 9 to adjusted recorder response. Make no further adjustment to the analyzer span control. Note: In Step 6, the O_3 response should be decreased by 90-95% of its new value. For example, if I_{40} = 45% chart and Z_A = 5% chart, the NO flow should be adjusted to yield an analyzer response of 7-9% chart.

STEP 13

Adjust the Input C gauge pressure to give a total air flow of approximately 5000 cm^3/min. Using a bubble flowmeter or wet-test meter, measure the total

air flow at the outlet of the calibration system. Record the total air flow (F_2), Input C pressure gauge setting (P_C), and the capillaries used on the data sheet. Calculate the diluted O_3 concentration ($[O_3]_{20}$) from:

$$[O_3]_{20} = [O_3]_{40} \times \frac{F_O}{F_2} \qquad \text{(Eq. 5)}$$

where $[O_3]_{20}$ = 20% URL O_3 concentration, ppm

$[O_3]_{40}$ = 40% URL O_3 concentration, ppm

F_O = original total air flow, cm^3/min

F_2 = total air flow after dilution, cm^3/min

Record the calculations and the recorder response (I_{20}) on the data sheet.

STEP 14: RECORDING RESULTS ON DATA SHEET

a. Record the O_3 concentrations generated and the analyzer responses obtained at these concentrations. Also record the zero and span settings before and after adjustments were made.

b. Plot the analyzer response (y axis) versus O_3 concentration (x axis) (see Figure A1). The analyzer response should be linear within ± 1%.

c. Summarize any problems encountered during the calibration. If this was a field calibration, name persons from local agencies present during the calibration.

d. Record on the O_3 analyzer recorder chart the name of the station calibrated, the date, information for each trace on the chart, and the time the calibration was begun. If possible, remove the calibration segment of the recorder chart and attach it to the data sheet. Advance the recorder chart, synchronize the time, and date it. If a portion of the recorder chart is removed, explain on remaining chart that a calibration took place. Do not destroy any ambient air data while cutting the chart.

SECTION 7

AUDIT PROCEDURE

If the Model 8861D Calibration System is used, it should be modified as described in Section 4. The flow conditions in the Bendix® Model 8861 Transportable Field Calibration Systems are optimized for this procedure and must be duplicated precisely to ensure the validity of the audit.

STEP 1

Record pertinent information about the analyzer being audited in the space provided on the data sheet (see Appendix B). If a request for information does not apply, write "N/A" in the space. In the margins, record any pertinent information needed for a particular analyzer but not specifically requested on the data sheet. Do not make any adjustments to the analyzer.

STEP 2

Connect the NO cylinder to the Bendix® Calibration System. Open the cylinder valve and let the NO flow rate stabilize. The pull-to-test valve for NO should be out while the O_3 generator and dilution air flow rates are measured. Place the sample manifold on the outlet of the calibration system.

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(See Figure 4 for the arrangement of the calibration apparatus.) Switch capillaries 1, 2, 3, and 4 of Input C (dilution air) to the "OFF" position. Set the air flow through the O_3 generator to 150-200 cm^3/min by adjusting the Input A gauge pressure. Measure the flow using a bubble flowmeter attached to the outlet of the calibration system. (The sample manifold must be disconnected each time a flow measurement is made at the outlet of the system.) Record the O_3 generator air flow (F_G) and the Input A pressure gauge setting (P_A) on the data sheet.

STEP 3

Set the total air flow to approximately 2500 cm^3/min by adjusting the Input C gauge pressure (any combination of capillaries 1, 2, 3, and 4 can be used). Using a bubble flowmeter or wet-test meter, measure the total air flow at the outlet of the calibration system. Record the total air flow (F_O), Input C pressure gauge setting (P_C), and capillaries used on the data sheet.

STEP 4

Advance the O_3 analyzer recorder chart a few inches from the last ambient air trace and allow the analyzer under audit to sample zero air from the calibration system for about 30 min or until a stable response is obtained. Record the unadjusted recorder response (Z_U) for audit zero air.

STEP 5

Switch the O_3 generator to the appropriate range and adjust the set point dial to provide an O_3 concentration of approximately 80% of URL as measured on the O_3 analyzer. Record the analyzer response (I_{80}) and the O_3 generator set point on the data sheet.

STEP 6

Add the NO flow and adjust the Input B pressure regulator until the O_3 analyzer response has been decreased by 90-95% of its original value. For example, if I_{80} = 85% chart and Z_U = 5% chart, the NO flow should be adjusted to yield an analyzer response of 9-13% chart. Record the analyzer response (I) after it has stabilized.

STEP 7

Measure the NO flow using a bubble flowmeter attached to the pull-to-test valve. Record the NO flow (F_{NO}), cylinder NO concentration (C_{NO}), and Input B pressure gauge setting (P_B) on the data sheet.

STEP 8

Calculate the exact NO concentration from:

$$[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} \qquad \text{(Eq. 1)}$$

where [NO] = NO concentration, ppm

F_{NO} = NO flow, cm^3/min

C_{NO} = cylinder NO concentration, ppm

F_O = total air flow, cm^3/min

Record the calculations on the data sheet.

STEP 9

Calculate the O_3 concentration from:

$$[O_3]_{80} = \frac{I_{80} - Z_U}{I_{80} - I} \times [NO] \qquad \text{(Eq. 2)}$$

where $[O_3]_{80}$ = 80% URL O_3 concentration, ppm

[NO] = NO concentration, ppm

I_{80} = original O_3 analyzer response, % chart

I = O_3 analyzer response after addition of NO, % chart

Z_U = unadjusted zero air recorder response, % chart

Record the calculations on the data sheet.

STEP 10

With the NO flow removed, the O_3 analyzer response should return to its original value (I_{80}). If the response does not return to within ± 1% of I_{80}, recheck I by adding NO to the system again. If I is exactly the same as before, remove the NO and let the O_3 response return to its new value. Record this new

response as I_{80} and recalculate $[O_3]_{80}$. If I is not the same as before, measure the NO flow again and recalculate [NO] and $[O_3]_{80}$. After the O_3 response has stabilized up-scale, record this new value as I_{80}. Calculate and record the percent audit error (PAE) from:

$$(PAE)_{80} = \frac{URL\ (I_{80} - Z_U)}{[O_3]_{80}} - 100 \qquad \text{(Eq. 3)}$$

where $(PAE)_{80}$ = percent audit error at 80% URL

URL = full scale range

I_{80} = original O_3 analyzer response, % chart

$[O_3]_{80}$ = 80% URL O_3 concentration, ppm

Z_U = unadjusted zero air response, % chart

STEP 11

Adjust the set point dial on the O_3 generator to give an O_3 concentration of approximately 50% of the URL and repeat Steps 5 through 10, substituting 40% URL for 80% URL, I_{40} for I_{80}, $[O_3]_{40}$ for $[O_3]_{80}$, and $(PAE)_{40}$ for $(PAE)_{80}$.

STEP 12: RECORDING RESULTS ON DATA SHEET

a. Record the O_3 concentrations generated and the analyzer responses and PAE values obtained at these concentrations.

b. Plot the analyzer response (y axis) versus O_3 concentration (x axis) (see Figure B1). The audit limits shown are ± 2% of full scale for zero and ± 15% difference between actual and observed values for up-scale readings.

c. Summarize any problems encountered during the audit. If this was a field audit, name persons from local agencies present during the audit.

d. Record on the O_3 analyzer recorder chart the name of the station audited, the date, information for each trace on the chart, and the time the audit was begun. If possible, remove the audit segment of the recorder chart and attach it to the data sheet. Advance the recorder chart, synchronize the time, and date it. If a portion of the chart is removed, explain on the remaining chart that an audit took place. Do not destroy any ambient air data while cutting the chart.

REFERENCES

1. Hodgeson, J. A., R. E. Baumgardner, B. E. Martin, and K. A. Rehme. Stoichiometry in the Neutral Iodometric Procedure for Ozone by Gas Phase Titration with Nitric Oxide. Anal. Chem., 43(8):1123-1126, 1971.

2. Rehme, K. A., B. E. Martin, and J. A. Hodgeson. Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide, and Ozone Analyzers by Gas Phase Titration. EPA-R2-73-246, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1974.

3. Rehme, K. A. Application of Gas Phase Titration in the Calibration of Nitric Oxide, Nitrogen Dioxide and Ozone Analyzers. In: Calibration in Air Monitoring, ASTM STP 598, American Society for Testing and Materials, 1976. pp. 198-209.

APPENDIX A

SAMPLE GPT-O_3 CALIBRATION DATA SHEET

1. STATION _____ CALIBRATION PERSONNEL _____

ADDRESS _____ _____

_____ DATE _____

Analyzer Calibrated _____ S/N _____

Ethylene Cylinder: Mfgr._____ S/N_____ Pressure _____psig

Ethylene Flow Rate _____cm^3/min

Sample Flow Rate _____cm^3/min

Zero Base Line _____% chart

Unadjusted Zero Setting _____.

Unadjusted Span Setting _____

Full Scale Range Selector Switch Position _____

Time Constant Selector Switch Position _____

Mode Selector Switch Position _____

Calibration System _____ S/N_____

NO Cylinder: Mfgr. ____ S/N ____ Pressure ____psig Conc. _____ppm

Room Temperature _____°C Barometric Pressure _____in Hg

NOTE: Refer to the "Ozone Calibration by Gas Phase Titration in Excess Ozone" procedure.

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2. O_3 Generator Flow: F_G

Vol. Meas. _____ cm^3 Time _____ min

F_G = ( )cm^3/( )min = _____ cm^3/min

Input A Pressure Gauge Setting: P_A = _____ % gauge

3. Total Air Flow: F_O

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_O = ( )cm^3/( )min = _____ cm^3/min

Input C Pressure Gauge Setting: P_C = _____ % gauge

Capillaries Used: 1 2 3 4 (Circle)

4. Zero Air Data

	Analyzer	Calibration
Unadjusted Recorder Response:		
Z_U:	_____	_____ % chart
Adjusted Recorder Response:		
Z_A:		_____ % chart

Adjusted Zero Setting: _____

5. 80% URL Data

O_3 Analyzer Recorder Response: I_{80} = _____ % chart

O_3 Generator Setting: _____

6. O_3 Analyzer Recorder Response (with NO present): I = _____% chart

7. NO Flow: F_{NO}

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_{NO} = ( )cm^3/( )min = _____cm^3/min

Cylinder NO Concentration: C_{NO} = _____ppm

Input B Pressure Gauge Setting: P_B = _____% gauge

8. $[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} = \frac{(\quad)(\quad)}{(\quad + \quad)} = \frac{(\quad)}{(\quad)} =$ _____ppm

9. $[O_3] = \frac{I_{80} - Z_A}{I_{80} - I} \times [NO] = \frac{(\quad - \quad)}{(\quad - \quad)} \times (\quad) = \frac{(\quad)(\quad)}{(\quad)} =$ _____ppm

$I_{80}(A) = \frac{[O_3]_{80} \times 100}{URL} + Z_A = \frac{(\quad \times 100)}{(\quad)} + (\quad) =$ _____% chart

10. Span Data

Unadjusted Recorder Response: I_{80} = _____% chart

Adjusted Recorder Response: $I_{80}(A)$ = _____% chart

Adjusted Span Setting: _____

11. 60% URL Data

New Total Air Flow: F_1

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_1 = ( )cm^3/( )min = _____cm^3/min

Input C Pressure Gauge Setting: P_C = _____% gauge

Capillaries Used: 1 2 3 4 (Circle)

$$[O_3]_{60} = [O_3]_{80} \times \frac{F_O}{F_1} = (\quad) \times \frac{(\quad)}{(\quad)} = _____ppm$$

O_3 Analyzer Recorder Response: I_{60} = _____% chart

12. 40% URL Data

O_3 Analyzer Recorder Response: I_{40} = _____% chart

O_3 Generator Setting: _____

O_3 Analyzer Recorder Response (with NO present): I = _____% chart

NO Flow: F_{NO}

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_{NO} = ( )cm^3/( )min = _____cm^3/min

Cylinder NO Concentration: C_{NO} = _____ppm

Input B Pressure Gauge Setting: P_B = _____% gauge

Input C Pressure Gauge Setting: P_C = _____% gauge

Capillaries Used: 1 2 3 4 (Circle)

$$[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} = \frac{(\quad)(\quad)}{(\quad + \quad)} = _____ppm$$

$$[O_3]_{40} = \frac{I_{40} - Z_A}{I_{40} - I} \times [NO] = \frac{(\quad - \quad)}{(\quad - \quad)} \times (\quad) = _____ppm$$

13. 20% URL Data

New Total Air Flow: F_2

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_2 = ( )cm^3/( )min = _____cm^3/min

Input C Pressure Gauge Setting: P_C = _____% gauge

Capillaries Used: 1 2 3 4 (Circle)

$$[O_3]_{20} = [O_3]_{40} \times \frac{F_O}{F_2} = (\quad) \times \frac{(\quad)}{(\quad)} = _____ppm$$

O_3 Analyzer Recorder Response: I_{20} = _____% chart

14. Results

a.

O_3 Concentration, ppm		Analyzer Response, % chart	
$[O_3]_O$ =	0.00	Z_A =	
$[O_3]_{20}$=		I_{20}=	
$[O_3]_{40}$=		I_{40}=	
$[O_3]_{60}$=		I_{60}=	
$[O_3]_{80}$=		I_{80}(A)=	

	Before Adjustment	After Adjustment
Zero Setting	_____	_____
Span Setting	_____	_____

b. (See Figure A1)

c. (Remarks)

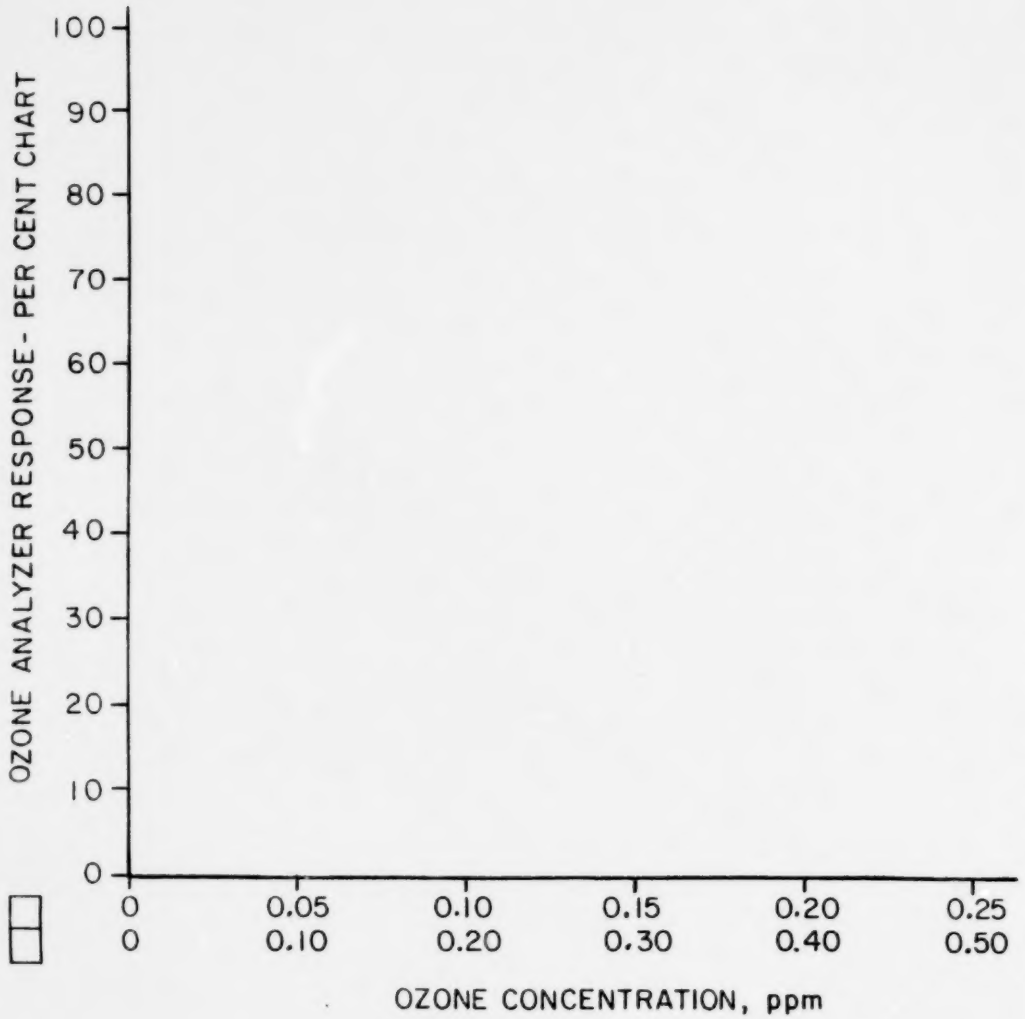

Figure A1. Calibration curve -- analyzer response versus O_3 concentration.

APPENDIX B

SAMPLE GPT-O_3 AUDIT DATA SHEET

1. STATION _____ AUDITOR _____

   ADDRESS _____ DATE _____

   _____

   Analyzer Audited _____ S/N _____

   Ethylene Cylinder: Mfgr. _____ S/N _____ Pressure _____psig

   Ethylene Flow Rate _____cm^3/min

   Sample Flow Rate _____cm^3/min

   Zero Base Line _____% chart

   Unadjusted Zero Setting _____

   Unadjusted Span Setting _____

   Full Scale Range Selector Switch Position _____

   Time Constant Selector Switch Position _____

   Mode Selector Switch Position _____

   Calibration System _____ S/N _____

   NO Cylinder: Mfgr. _____ S/N _____ Pressure ____psig Conc. ____ppm

   Room Temperature _____°C Barometric Pressure _____in Hg

   NOTE: <u>This is an audit</u>. <u>Do not make any adjustments to the analyzer</u>. (Refer to the "Ozone Audit by Gas Phase Titration in Excess Ozone" Procedure.)

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2. O_3 Generator Flow: F_G

Vol. Meas. _____cm^3 Time _____min

F_G = ( )cm^3/( )min = _____cm^3/min

Input A Pressure Gauge Setting: P_A = _____% gauge

3. Total Air Flow: F_O

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_O = ( )cm^3/( )min = _____cm^3/min

Input C Pressure Gauge Setting: P_C = _____% gauge

Capillaries Used: 1 2 3 4 (Circle)

4. Unadjusted Recorder Response: Z_U = _____% chart (audit zero air)

5. 80% URL O_3 Data

O_3 Analyzer Recorder Response: I_{80} = _____% chart

O_3 Generator Setting: _____

6. O_3 Analyzer Recorder Response (with NO present): I = _____% chart

7. NO Flow: F_{NO}

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_{NO} = ( )cm^3/( )min = cm^3/min

Cylinder NO Concentration: C_{NO} = _____ppm

Input B Pressure Gauge Setting: P_B = _____% gauge

8. $[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} = \frac{(\quad)(\quad)}{(\quad + \quad)} = \frac{(\quad)}{(\quad)} =$ _____ppm

9. $[O_3]_{80} = \frac{I_{80} - Z_U}{I_{80} - I} \times [NO] = \frac{(\quad - \quad)}{(\quad - \quad)} \times (\quad) = \frac{(\quad)(\quad)}{(\quad)} =$ _____ppm

10. Recorder Response: I_{80} = _____% chart

$(PAE)_{80} = \frac{URL\ (I_{80} - Z_U)}{[O_3]_{80}} - 100 = \frac{(\quad)(\quad - \quad)}{(\quad)} - 100 =$ _____%

11. 40% URL O_3 Data

O_3 Analyzer Recorder Response: I_{40} = _____% chart

O_3 Generator Setting: _____

O_3 Analyzer Recorder Response (with NO present): I = _____% chart

NO Flow: F_{NO}

	Time (min)	Avg. Time (min)	Vol. Meas. (cm^3)
1)	_____	_____	_____
2)	_____		
3)	_____		

F_{NO} = ( )cm^3/( )min = _____cm^3/min

Cylinder NO Concentration: C_{NO} = _____ppm

Input B Pressure Gauge Setting: P_B = _____% gauge

$$[NO] = \frac{F_{NO} \times C_{NO}}{F_{NO} + F_O} = \frac{(\quad)(\quad)}{(\quad + \quad)} = \frac{(\quad)}{(\quad)} = _____ppm$$

$$[O_3]_{40} = \frac{I_{40} - Z_U}{I_{40} - I} \times [NO] = \frac{(\quad - \quad)}{(\quad - \quad)} \times (\quad) = \frac{(\quad)(\quad)}{(\quad)} = _____ppm$$

Recorder Response: I_{40} = _____% chart

$$(PAE)_{40} = \frac{URL\ (I_{40} - Z_U)}{[O_3]_{40}} - 100 = \frac{(\quad)(\quad - \quad)}{(\quad)} - 100 = _____\%$$

12. Results

a.

O_3 Concentration, ppm		Analyzer Response, % Chart		PAE
$[O_3]_O$ =	0.000	Z_U =		
$[O_3]_{40}$ =		I_{40} =		___
$[O_3]_{80}$ =		I_{80} =		___

b. (See Figure B1).

c. (Remarks)

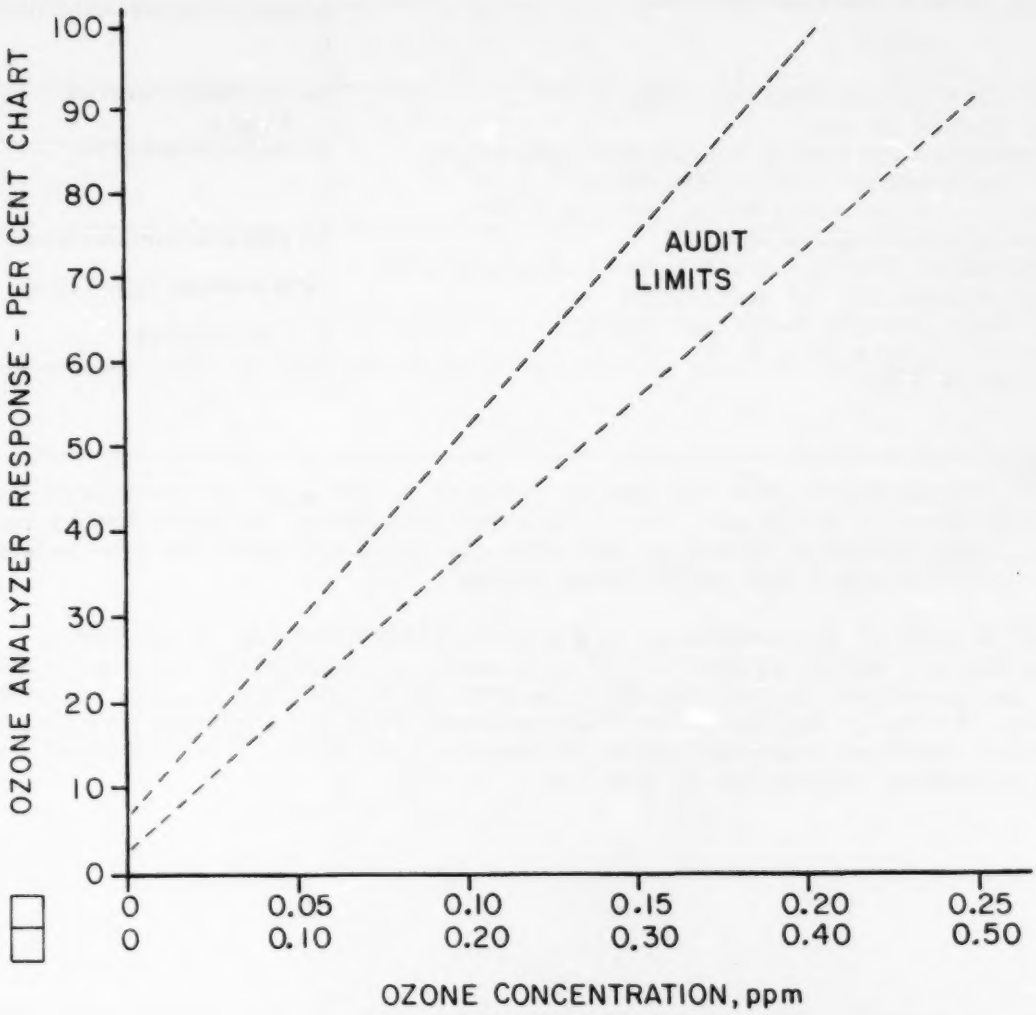

Figure B1. Audit curve — analyzer response versus O_3 concentration.